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(54) Title: METAL FOAM FOR SECONDARY BATTERY ELECTRODE

(57) Abstract

A copper metal foam, or a large pore size metal foam, particularly a large pore size nickel metal foam, is utilized as a support for a negative electrode in a metal hydride alkaline secondary battery. Or a copper metal foam is employed as a support for an electrode of alithium–ion secondary battery. The metal foam for the electrode support is a light weight, typically very flexible foam. The metal foam is particularly serviceable as an electrode support for a hydrogen storage alloy negative electrode, e.g., an electrode containing an active material of metallic alloy, such as an AB_5 class of alloy or an AB_2 class of alloy. As a support for an alkaline secondary battery negative electrode, the large pore metal foam may also serve as the negative cadmium electrode for a nickel–cadmium battery. As copper metal foam, the foam may further serve as the support for the positive or negative electrode, or for both, for a lithium–ion secondary battery.

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METAL FOAM FOR SECONDARY BATTERY ELECTRODE

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/030786, filed November 13, 1996.

TECHNICAL FIELD

This invention relates to copper metal foam, or a large pore size metal foam that is used as an electrode support in a metal hydride alkaline secondary battery. The support, as a large pore size metal foam, can also serve as the negative electrode for a nickel-cadmium battery. Further, the support as a copper metal foam can be utilized in a lithium-ion battery.

A metal hydride alkaline secondary battery, such as a rechargeable sealed nickel-metal hydride battery, uses hydrogen, absorbed in a metal alloy for the active negative material to provide the negative electrode. The active material for the electrode is usually made into a paste. It has been traditional to then follow a process which introduces the paste into a three-dimensional structure usually of the foam type. The foam forms the electrode support, or substrate, for the electrode. It has been taught to use a nickel foam for the negative electrode of a nickel-metal hydride battery. It is also taught to use nickel foams of small mean cell diameter for the foam. Traditionally, nickel foams of small mean cell diameter on the order of 100 pores per inch (ppi) have been found useful.

For example, in U.S. Patent No. 5,532,076 directed generally to batteries made with hydrogen storage electrodes where the negative electrode contains a special hydrogen storage alloy or a hydride thereof, it is taught to form an electrode using a mixture containing the alloy filled into a porous foam nickel sheet. The nickel sheet has a mean pore size of about 425 microns, or about 110 ppi for the sheet.

Recently, however, much effort for these negative electrodes has been directed toward perforated plate electrode supports. These are supports for the negative electrode. They can be a perforated nickel plate. The plates can have active material applied to both sides of the plate.

For example, in U.S. Patent No. 5,529,857, it is taught to take a hydrogen-absorbing alloy powder and prepare it in a slurry. The slurry is then applied on both sides of a perforated metal plate and the plates with the slurries are dried to provide a hydrogen-absorbing alloy electrode.

Similarly, in U.S. Patent No. 5,525,435, a metal hydride as a hydrogen storage material, which material is of fine particle size, is formed into a mix. The mix is gravimetrically embedded into a perforated nickel-plated carrier.

This recent development utilizing ostensibly low-cost metal, e.g., perforated metal plate of nickel plated steel, has been replacing the foamed nickel porous material previously used as an electrode support. The metal support sheets can be made of, or covered with, a metal, as represented by the nickel plated perforated steel. With this recent trend toward perforated collectors for the negative electrode, there is still, however, room for improvement in regard to characteristics such as ease of manufacture of the electrode. Moreover, the newer electrode supports such as of the punched metal type, lack desirable three-dimensional structure and can exhibit a low ability to hold an active material. There is thus room for improvement for better adherence of the hydrogen storage alloy, as applied such as in paste form to the electrode support.

Along the same line, for lithium-ion batteries, the current collectors, or supports, have been metal plates, supplied as metal foil. As electrodes, the foil can delaminate from the active material. These foil supports, lacking a three-dimensional structure, have a tendency toward a reduced ability to hold an active material. There is, therefore, room for improvement in such a battery system for providing better adherence, particularly for the negative electrode, of the active material to the support.

DISCLOSURE OF INVENTION

Accordingly, it is an object of the present invention to provide an improvement in the negative electrode for a hydrogen storage alloy electrode where an active material, such as in a paste or slurry form, is applied to an electrode support.

It is also an object of the invention to provide such improvement in an electrode, usually the negative electrode, for a lithium-ion battery, where an active material, which may also be in a paste or slurry form, is applied to an electrode support.

It is an object of the present invention to provide for ease of manufacture of such negative electrodes and to provide for enhanced adherence of the active material to the electrode substrate.

Another object of the present invention is to provide an improved electrode for a storage battery, such as a hydrogen storage alloy electrode, using a hydrogen storage alloy powder.

An additional object of the present invention is to furnish an improved electrode for a lithium-ion battery, such as the negative electrode, employing a lithiated carbon intercalation material.

It is also an object of the present invention to provide an improved electrode as a negative cadmium electrode in a nickel cadmium battery.

Another object of the invention is to provide for an improved electrode for a storage battery and a higher battery capacity.

In one aspect, the invention pertains to a negative, hydrogen-absorbing metal alloy electrode for a metal hydride alkaline, secondary battery, such negative electrode having a support comprising a copper metal foam support member.

In another aspect, the invention pertains to an electrode for a lithium-ion secondary battery, with the electrode having a support comprising a copper metal foam support member.

In a further aspect, the invention is directed to a large pore size metal foam support member for an alkaline secondary battery, the foam having a pore size of larger than about 80 pores per inch and a weight of less than about 500 grams per square meter, with the substrate having a thickness within the range from about 0.75 millimeter to about 3 millimeters.

In a specific aspect, the electrode is the cadmium electrode for a nickel-cadmium battery, and the electrode has the large pore size support member as described hereinabove.

In another specific aspect, the invention relates to negative electrodes for alkaline secondary batteries with the electrodes having large pore nickel metal foam supports, which large pore nickel metal supports have parameters as described hereinabove.

The foam substrate is filled with an active negative material. The filling, such as for a nickel-metal hydride battery, can be a hydrogen storage material and the foam substrate can be filled such as by first forming a paste or slurry containing active negative material. This mix is then impregnated into the foam substrate. The resulting article may then proceed through further processing steps, e.g., a compression step, to form a finished battery negative electrode.

Thus, in a further aspect, the invention is directed to a method of producing a negative electrode for an alkaline secondary battery, comprising the steps of:

providing a large pore metal foam negative electrode support member, with the support member having a pore size of larger than about 80 pores per inch and a weight of less than about 420 grams per square meter;

establishing such large pore metal foam in sheet form, with the resulting sheet form electrode support member having a thickness within the range from about 0.75 millimeter to about three millimeters; and

introducing active negative material into the sheet form electrode support member of large pore metal foam to produce a filled foam negative electrode in sheet form.

In a still further aspect, the invention is directed to the method as described hereinabove, but utilizing specifically a large pore nickel metal foam electrode support member having parameters as described hereinbefore.

In yet a further aspect, the invention is directed to the method described hereinabove, but utilizing a copper metal foam that is not limited to

a large pore size, as an electrode support member in a metal hydride alkaline secondary battery.

In another aspect, the invention is directed to the method described hereinabove, but again utilizing a copper metal foam that is not limited to a large pore size, with the foam having a thickness of from at least about 0.5 millimeter, as an electrode support member in a lithium-ion battery.

BEST MODE FOR CARRYING OUT THE INVENTION

A negative electrode for an alkaline secondary battery can contain a hydrogen storage material. A representative such battery is a sealed nickel-metal hydride battery. For such batteries, two types of metallic alloys are generally used. One type of hydrogen storage material is the AB_2 type hydrogen storage alloy. This class of alloys contains titanium and zirconium. Another class of alloy is the AB_5 class of alloys. These are the rare-earth (Misch metal) alloys. They are based on lanthanum nickel. These alloys will be discussed in greater detail hereinbelow. For both classes of alloys, some of the base metals can be replaced with other metals to achieve various battery characteristics. Representative hydrogen storage materials useful in negative electrodes of alkaline secondary batteries have been discussed, for example, in U.S. Patent No. 5,525,435.

It is also contemplated that the negative electrode for the alkaline secondary battery may be such as is useful in a nickel-cadmium battery. For such a battery, the active material for the negative electrode, in the charged state, is a cadmium active material comprising cadmium metal.

In a lithium-ion battery, there can be used a lithiated carbon intercalation material for the negative electrode. For the positive active material, there may be used a lithiated transition metal intercalation compound. Compounds for such service will be discussed more particularly hereinbelow.

As used herein, the term "support member", or sometimes for convenience just "support", refers to the electrically conductive metal foam to which there is applied an active material, e.g., a negative active material to form a negative electrode that can be utilized in a battery. Such support may

sometimes be referred to herein as a "substrate" or "collector", as in "current collector". For preparing the support member such as a copper metal foam electrode support member, there can initially be used a reticulate, three-dimensional precursor form, e.g., a polyurethane foam. This can be processed by electrolessly, then electrolytically, depositing copper onto the precursor form. Useful polymeric foams are particularly advantageous as the precursor form reticulated material, for economy. Those which may be employed include polymeric foams such as polyester polyurethane foam, polyesters and olefin polymers. Examples of commercially available preferred organic polymer substrates include polyurethane foams marketed by Foamex International, Inc., including polyether-polyurethane foams, and polyester polyurethane foams.

It will be understood that non-foam materials may also be employed as precursor form materials. Filaments, including fibers or threads, may serve as a substrate for the deposition of an electroconductive metal, as disclosed in U.S. Patent 4,370,214. An open-cell organic or inorganic foam or sponge, prepared using a "pore-former", e.g., discrete "pore-former" beads, pellets and the like, has been disclosed in U.S. Patent 4,517,069. Such technique can be utilized in making a metal foam precursor which may be converted to a metal foam as by heat application.

The precursor form reticulate material may have some electrical conductivity. For a polymer foam, this can be achieved by employing any of a number of well-known procedures such as coating with a latex graphite; coating with a metal powder as described in U.S. Patent 3,926,671; electroless plating with a metal such as copper or nickel; sensitizing by application of a metal such as nickel as described in U.S. Patent 4,370,214; coating with an electrically conductive paint, e.g., a paint containing carbon powder, or a metal powder such as copper powder; coating of a pore-former as described in U.S. Patent 4,517,069; and vacuum deposition of a metal by cathode sputtering with a metal or alloy as disclosed in U.S. Patent 4,882,232.

A continuous production process for preparing a porous metal article in sheet form using an open-cell foam sheet, such as a polymeric foam sheet, as a starting material, and using electroplating in the process has been taught in U.S. Patent 4,978,431. Such a process can be particularly suitable for preparing a nickel metal foam. A large pore nickel metal foam electrode support is also contemplated as particularly useful herein. But most often, the copper metal foam electrode support is preferred, except in use with the AB_2 type hydrogen storage alloy where large pore nickel metal foam is advantageous for best electrode stability. However, for convenience, the copper metal foam will generally be referred to hereinafter. In addition to the above-mentioned continuous production process, U.S. Patent 5,300,165 proposes a similar method for the manufacture of metallic porous sheets from mesh sheets and non-woven fabric sheets, which can be layered together.

Generally, if electroplating has been utilized, after the completion of the plating, the resulting metallized article can be washed, dried, and may be thermally treated, e.g., to decompose a polymer core substance. In some instances, the article may be annealed, such as in a reducing or inert atmosphere. Regarding thermal decomposition, the specification of U.S. Patent 4,687,553 suggests a multi-stage heat decomposition method. According to the patent, when nickel is plated, thermal decomposition is conducted at a temperature in the range of about 500°C-800°C for up to about three hours depending on the plastic foam (polymer core substance) used. Such thermal treatment could also be carried out on a copper foam to decompose a polymer core substance. The temperature of such treatment could also be in the range of 500°C-800°C. Annealing may also be used with the foam. For copper foam, an annealing temperature in the range of 700°C-1,000°C can be serviceable, and can be carried out for a time of from about five minutes to about two hours. Annealing can be carried out by any ordinary method. For example, in the case of nickel, it is carried out in a hydrogen atmosphere at a temperature in the range of from about 800°C to

about 1200°C, again for a time of from about five minutes to about two hours.

The large pore metal foam support member, particularly when it is a large pore nickel foam support member, or when the copper foam support member is to be used as a large pore foam support member, should have a pore size of larger than on the order of about 80 pores per inch (ppi), e.g., a pore size that is at least larger than about 500 microns (although it will be understood that some foam commercially qualified at 80 ppi may have a pore size as large as 600 microns). It will also be understood that a lower ppi equates to a larger pore size. Advantageously, for ease of filling of active negative material within the large pore metal foam support, as well as desirable flexibility for the support, such support will have a pore size within the range from about 40 ppi to about 70 ppi. Preferably, for best ease of filling, plus best support flexibility, as well as further for the characteristic of a small bending radius, the pore size will be within the range from about 50 ppi to about 60 ppi.

Where the support member is not a large pore metal foam support member, which will be a copper foam support member, such support member can have a pore size larger or smaller than about 80 ppi. In the application of a copper support member for a lithium-ion secondary battery, where the copper foam can be in sheet form and have a reduced thickness, as more particularly discussed hereinbelow, it can be advantageous for enhanced mechanical flexibility for the foam to have a smaller pore size than about 80 ppi. Thus, the pore size for such foam application can be on the order of about 130 ppi or even smaller. In such application, the copper foam support member typically has a pore size providing a range of pores per inch from about 70 ppi to about 110 ppi, or more.

In battery construction, typically for cylindrical, button and prismatic configured batteries, the support member will be in a planar, e.g., a plate-like, or more typically sheet, form having a thickness dimension which is less than its width or length. In these constructions, usually referred to herein for convenience simply as "sheet form", a substrate can generally have a sheet

thickness within the range from about 0.75 millimeter to about three millimeters (mm) and preferably within the range from about one mm to about two mm, e.g., a sheet thickness of 1.5 mm. However. for application of copper metal foam in lithium-ion batteries, the sheet thickness may be a reduced thickness of as little as about 0.5 mm. With such sheet thickness, particularly the copper metal foam support member has a highly desirable flexibility, e.g., a coilability that achieves a tightly coiled electrode that may be crack-free, such as for providing a negative electrode in a cylindrical battery configuration. Particularly in the sheet form, the support member can have a bending radius within the range from about 0.2 centimeter to about 0.3 centimeter. With such flexibility, the support can not only be utilized in a cylindrical configuration, but can also be employed in coiled configuration. It will be understood that these above-discussed sheet thicknesses are thicknesses before any sheet compression, e.g., compression achieved as by calendering the sheet. Where such compression has been used, the sheet may then typically have a thickness within the range of from about 0.1 mm to about 1.5 mm.

Within these above-discussed parameters, and advantageously, for the highest electrode loading of active material, such support member in sheet form as a large pore support member, and particularly as a nickel foam support member, can have a weight within the range from about 200 to less than about 700 grams per square meter, but typically less than about 500 grams per square meter. When considering a copper metal foam support member, and particularly such a member of any pore size, the member will generally have a weight within the range of from about 150 or less, e.g., 80 or 100, up to 500 grams per square meter. Preferably, for best loading as well as overall battery economy, the copper metal support member will have a weight within the range from about 100 to about 400 grams per square meter. Similarly, in some applications it can be advantageous for the large pore nickel foam to have a weight of less than about 400 grams per square meter.

The copper metal of the support is most always simply a readily commercially available copper metal for best electrical conductivity of the electrode support member. However. it is contemplated to use copper alloy or intermetallic mixtures of copper with other metals. Typical alloying metals, as well as metals for mixing with copper, include nickel, zinc, tin, aluminum, beryllium and iron. Moreover, the nickel metal of the support is most always simply a readily commercially available nickel metal for best economy of the electrode support. However, it is contemplated to use nickel alloy or intermetallic mixtures of nickel with other metals. Typical alloying and mixing metals with nickel include copper, cobalt, chromium, iron, molybdenum and aluminum.

For preparing an electrode, for the active negative material as a hydrogen storage material, it is contemplated to use the AB_2 type hydrogen storage alloy, but there will most always be used an AB_5 type hydrogen storage alloy, which have been mentioned hereinbefore. In the AB_2 type, A can be an element with a large affinity for hydrogen such as Zr or Ti, and B is a transition metal such as Ni, Mn or Cr. Members of the AB_2 class of hydrogen absorbing materials may also include the binary $ZrCr_2$, ZrV_2 and $ZrMo_2$, although all of this class of hydrogen-absorbing material are contemplated as being useful in the present invention. The AB_5 class of alloys can be referred to as the rare-earth (Misch metal) alloys based around lanthanum nickel. Thus, A can be represented by lanthanum, while B might be as defined above. The AB_5 type negative materials for battery negative electrodes are well known and many materials are described in the prior art. All such hydrogen storage alloys are contemplated as useful in preparing a negative electrode of the present invention. For a nickel-cadmium battery, the negative electrode cadmium active material will comprise cadmium metal.

For preparing an electrode with active material for a lithium-ion secondary battery, there will most always be prepared a negative electrode or anode. The active material can be a lithiated carbon intercalation material. Carbon materials, which may be in powder form, and are appropriate choices for this anode material, can include petroleum coke,

graphite and other types of carbon. However, it is also contemplated that the copper foam support member may be useful for the cathode, i.e., positive electrode, of the cell. In this application, the copper foam will contain a lithium insertion compound such as $LiCoO_2$ or other lithiated metal oxide compound for the active material.

Regardless of the active material utilized, such material will generally be made into a paste or slurry. This can typically be done using water or, particularly for a lithium-ion electrode, using an organic solvent, e.g., polyvinylidene fluoride. It is also contemplated to use dry, finely divided active negative material. In forming a paste or slurry, the active negative material will typically be finely divided, e.g., have an average particle size within the range from about 25 microns to about 200 microns, but more generally within the range from about 75 to 100 microns. For a hydrogen-absorbing alloy powder, such finely divided material can be blended as by kneading or mixing with a solution also containing a binder or thickener. Useful binders, or thickeners, for the alloy powders can include polymeric binders, such as polyvinyl alcohol or hydroxypropyl cellulose or carboxymethyl cellulose. Serviceable liquids for supplying the mix medium with these alloy powders will include water or an organic solvent. The paste or slurry is then introduced into the electrode support member, such as by any process for introducing a paste or slurry material into a foam type substrate, e.g., spray application, or pressure application, or vacuum application.

The electrode support member impregnated with the active negative material, typically introduced as a paste or slurry, can then proceed through any of those additional steps that are useful for final preparation of an electrode, e.g., drying, which can remove volatile substituents from a paste or slurry. Such steps could also include a sintering step, as for providing sintering of a finely divided alloy powder. For the electrode having a large pore nickel metal foam support, a sintering step could be carried out at a temperature within the range from about 800°C to about 1,200°C. However, where the electrode support member is a copper metal foam, such a

sintering step would be carried out at a temperature within the range from about 700°C to about 1,000°C. With either support member, such sintering could proceed for a time of from a few minutes, e.g., about five minutes, to about two hours. An additional step for final preparation of the electrode, which could be employed such as after drying or sintering, or after both, would be an electrode compression step. Usually, such compression would be in the direction of the thickness of the filled foam sheet and could be achieved such as by rolling the filled foam sheet. Such compression could be utilized to provide a controlled sheet thickness. The compression, as for an electrode in sheet form having the copper metal foam support member, could be carried out at an exemplary pressure of about five tons per square centimeter (tons/cm^2) of electrode sheet area. More generally, such compression might be carried out at a pressure within the range from about one to about 10 tons/cm^2 of electrode sheet area.

In battery preparation, for either the nickel-metal hydride secondary battery or the nickel-cadmium secondary battery, any of the positive electrodes as are conventional or as are contemplated for use in the battery, will be useful in the present invention. Typically, such a positive electrode will contain a positive active material, usually composed of a metal oxide, in a support. A representative positive active material comprises nickel oxyhydroxide, and a serviceable support is frequently a nickel foam. For a lithium-ion battery, the copper foam support may particularly be used for the positive (cathode) electrode and it can be useful to employ an aluminum foil as the support for the negative (anode) electrode. Representative negative active materials have been discussed hereinbefore.

Electrodes in the battery can be separated with a usually synthetic, typically non-woven material. The separator may serve as an insulator between electrodes as well as a medium for absorbing an electrolyte, e.g., an alkali electrolyte. A representative separator material is a nylon or a polypropylene non-woven fabric. The polypropylene fabric could be of sulfonated polypropylene. The separator may have, for example, on the order of a 60 percent to 70 percent porosity. A serviceable electrolyte

solution for a nickel metal hydride battery can be an aqueous potassium hydroxide solution. Such solution may contain lithium hydroxide, e.g., a 35 percent Li-KOH electrolyte solution.

The electrodes, including those as may be set apart by the separator, are assembled in any conventional manner, e.g., spirally wound together as a sandwich with the separator as the middle material. The assembly in winding can be coiled under pressure, such as a pressure between about 4 and about 8 tons per square centimeter of the electrode sheet surface area. The assembly could then be utilized in a cylindrical cell battery. Other serviceable battery constructions include button cells and prismatic cell batteries.

As an illustrative embodiment representative of the present invention, a large pore copper metal foam sheet is prepared using the technique as disclosed in Example 1 of U.S. Patent No. 5,374,491. The large pore copper metal foam sheet has a 1.5 mm thickness. From this sheet, there is obtained sections, that are each 145 mm in width (Y-axis) and 290 mm in length (X-axis), to serve as copper metal foam support members. The copper metal foam support members each have large pores, larger than 80 pores per inch. The measurement of pore size is carried out in accordance with the procedure disclosed in U.S. Patent No. 5,374,491. The support members have a weight of about 400 grams per square meter. The highly flexible and large pore copper metal foam support members have a bending radius of less than 0.3 centimeter.

A commercially available hydrogen storage alloy of the AB_5 type (Misch metal) is provided as a powder having a particle diameter less than about 150 mesh (U.S. Sieve Series). A paste with this alloy powder is prepared using a one weight percent aqueous solution of carboxymethyl cellulose. The paste is introduced into the large pore copper metal foam support members and dried.

One resulting filled sheet is rolled in the X-axis direction at a pressure of 5 tons per square centimeter to provide a tightly coiled sheet. No cracking of the sheet is observed during such operation.

Separately, a positive electrode utilizing a nickel foam sheet having an 0.5 mm thickness is fabricated using a nickel oxyhydroxide filling. A second, filled, large pore copper metal foam support member, prepared as described hereinabove, is placed as the negative electrode on one side of a nylon separator, and the positive electrode sheet is placed on the opposite side of the separator. The separator has an 0.18 mm thickness and 65 percent porosity. This assembly is then coiled at a pressure of 5 tons per square centimeter around the X-axis direction of the negative electrode sheet to obtain a power generation assembly. By visual inspection, the coiled assembly is seen to be free from cracking for the coiled copper metal foam support member of the assembly.

CLAIMS

1. A negative, hydrogen-absorbing metal alloy electrode for a metal hydride alkaline secondary battery, said negative electrode having a support comprising a copper metal foam support member.

2. The electrode of claim 1 wherein said support member is a large pore support member having a pore size of larger than about 80 pores per inch and a weight of less than about 500 grams per square meter, said support member having a thickness within the range from about 0.75 millimeter to about three millimeters.

3. The electrode of claim 1 wherein said copper metal foam support member is in flexible, sheet form.

4. The electrode of claim 3 wherein said flexible copper metal foam in sheet form has a thickness less than about two millimeters.

5. The electrode of claim 4 wherein said flexible copper metal foam has a bending radius within the range from about 0.2 centimeter to about 0.3 centimeter.

6. The electrode of claim 2 wherein said large pore copper metal foam support member has a weight within the range from about 100 grams per square meter to about 500 grams per square meter.

7. The electrode of claim 2 wherein said large pore copper metal foam support member has a pore size within the range from about 40 pores per inch to about 60 pores per inch.

8. The electrode of claim 1 wherein said copper metal foam support member comprises a metal of copper, copper alloy, or intermetallic mixture of copper including copper alloys containing metals such as nickel, zinc, tin, aluminum, beryllium and iron.

9. The electrode of claim 1 wherein said copper metal foam support member contains a hydrogen-absorbing metal alloy or hydride thereof and said alloy comprises one or more of an AB_2 type hydrogen storage alloy or an AB_5 type hydrogen storage alloy.

10. The electrode of claim 9 wherein said large pore copper metal foam support member contains an active negative material comprising a finely

divided alloy powder having an average particle size within the range from about 25 microns to about 200 microns.

11. A metal hydride alkaline secondary battery containing the electrode of claim 1 as a negative electrode.

12. A negative cadmium electrode for a nickel-cadmium alkaline secondary battery, said negative electrode having a support comprising a large pore copper metal foam support member having pore size greater than about 80 pores per inch, with said support member having a thickness of within the range from about 0.75 millimeter to about three millimeters.

13. The electrode of claim 12 wherein said large pore copper metal foam support member is in flexible, sheet form.

14. The electrode of claim 13 wherein said flexible copper metal foam in sheet form has a thickness less than about two millimeters.

15. The electrode of claim 13 wherein said flexible copper metal foam has a bending radius within the range from about 0.2 centimeter to about 0.3 centimeter.

16. The electrode of claim 12 wherein said copper metal foam support member has a weight within the range from about 100 grams per square meter to about 500 grams per square meter.

17. The electrode of claim 12 wherein said large pore copper metal foam support member has a pore size within the range from about 40 pores per inch to about 60 pores per inch.

18. The electrode of claim 12 wherein said copper metal foam support member comprises a metal of copper, copper alloy, or intermetallic mixture of copper including copper alloys containing metals such as nickel, zinc, tin, aluminum and iron.

19. The electrode of claim 12 wherein said support contains a cadmium active material in finely divided form.

20. The electrode of claim 19 wherein said cadmium active material in finely divided form comprises cadmium metal and has an average particle size within the range from about 10 microns to about 200 microns.

21. A nickel-cadmium alkaline secondary battery containing the electrode of claim 12 as a negative electrode.

22. An electrode for a lithium-ion secondary battery, said electrode having a support comprising a copper metal foam support member.

23. The electrode of claim 22 wherein said support member has a pore size on the order of from about 60 pores per inch to smaller than about 130 pores per inch and a weight of less than about 500 grams per square meter, said support member having a thickness within the range from about 0.5 millimeter to about three millimeters.

24. The electrode of claim 22 wherein said copper metal foam support member is in flexible, sheet form.

25. The electrode of claim 24 wherein said flexible copper metal foam in sheet form has a thickness less than about one millimeter and a weight of less than 300 grams per square meter.

26. The electrode of claim 24 wherein said copper metal foam support member has a weight of more than about 80 grams per square meter and a thickness of less than about two millimeters.

27. The electrode of claim 22 wherein said copper metal foam support member comprises a metal of copper, copper alloy, or intermetallic mixture of copper including copper alloys containing metals such as nickel, zinc, tin, aluminum, beryllium and iron.

28. The electrode of claim 22 wherein said copper metal foam support member is for a negative lithium-ion battery electrode and said support member contains lithiated carbon.

29. The electrode of claim 22 wherein said copper metal foam support member is for a positive lithium-ion battery electrode and contains lithiated metallic oxide.

30. A lithium-ion secondary battery containing the electrode of claim 22 as one or more of a negative electrode or a positive electrode.

31. A negative, hydrogen-absorbing metal alloy electrode for a metal hydride alkaline secondary battery, said negative electrode having a support comprising a large pore nickel metal foam support member having pore size

larger than about 80 pores per inch, with a weight of less than about 700 grams per square meter, said support member having a thickness within the range from about 0.75 millimeter to about three millimeters.

32. The electrode of claim 31 wherein said large pore nickel metal foam support member is in flexible, sheet form.

33. The electrode of claim 32 wherein said flexible large pore nickel metal foam in sheet form has a thickness less than about two millimeters.

34. The electrode of claim 31 wherein said flexible nickel metal foam has a bending radius within the range from about 0.2 centimeter to about 0.3 centimeter.

35. The electrode of claim 31 wherein said large pore nickel metal foam support member has a pore size within the range from about 40 pores per inch to about 60 pores per inch.

36. The electrode of claim 31 wherein said large pore nickel metal form support member has a weight within the range from about 200 grams per square meter to about 400 grams per square meter.

37. The electrode of claim 31 wherein said large pore nickel metal foam support member comprises a metal of nickel, nickel alloy, or intermetallic mixture of nickel including nickel alloys containing metals such as copper, cobalt, chromium, iron, molybdenum and aluminum.

38. The electrode of claim 31 wherein said large pore nickel metal foam support member contains a hydrogen-absorbing metal alloy or hydride thereof and said alloy comprises one or more of an AB_2 type hydrogen storage alloy or an AB_5 type hydrogen storage alloy.

39. The electrode of claim 31 wherein said large pore nickel metal foam support member contains an active negative material comprising a finely divided alloy powder having an average particle size within the range from about 25 microns to about 200 microns.

40. A metal hydride alkaline secondary battery containing the electrode of claim 31 as a negative electrode.

41. A negative cadmium electrode for a nickel-cadmium alkaline secondary battery, said negative electrode having a support comprising the large pore nickel metal foam support member of claim 31.

42. A nickel-cadmium alkaline secondary battery containing the electrode of claim 41 as a negative electrode.

43. A method of producing a negative electrode for a metal hydride alkaline secondary battery, comprising the steps of:

providing a copper metal foam negative electrode support member;

establishing said copper metal foam in sheet form, with the resulting sheet form electrode support member having a thickness within the range from about 0.75 millimeter to about three millimeters; and

introducing active negative material into said sheet form electrode support member of copper metal foam to produce a negative electrode in sheet form containing said material in said sheet.

44. The method of claim 43 wherein there is provided a large pore copper metal foam negative support member having a pore size of larger than about 80 pores per inch and a weight of less than about 420 grams per square meter.

45. The method of claim 43 further comprising drying the filled foam sheet to remove volatile substituents from the active negative material introduced into said support member.

46. The method of claim 43 including introducing active negative material containing finely divided hydrogen-absorbing alloy powder into said sheet of copper metal foam.

47. The method of claim 46 wherein there is introduced active negative material into said electrode support member that comprises one or more of AB_2 type hydrogen storage alloy, AB_5 type hydrogen storage alloy, or a cadmium active material comprising cadmium metal.

48. The method of claim 46 wherein said finely divided alloy powder is sintered and said sintering is carried out at a temperature between about

700°C to about 1000°C for a time of from about five minutes to about two hours.

49. The method of claim 43 wherein said active negative material is introduced into said sheet member of copper metal foam by one or more of spray application, or pressure or vacuum application.

50. The method of claim 43 further comprising compressing said filled foam sheet in the direction of the thickness thereof.

51. A negative electrode for a metal hydride alkaline secondary battery produced by the method of claim 43.

52. A method of producing an electrode for a lithium-ion secondary battery, comprising the steps of:

providing a copper metal foam electrode support member;

establishing said copper metal foam in sheet form, with the resulting sheet form electrode support member having a thickness within the range from about 0.5 millimeter to about three millimeters; and

introducing active material into said sheet form electrode support member of copper metal foam to produce an electrode in sheet form containing said material in said sheet.

53. The method of claim 52 wherein there is provided a copper metal foam support member having a pore size on the order of from about 60 pores per inch to smaller than about 110 pores per inch and a weight of less than about 500 grams per square meter.

54. The method of claim 52 further comprising drying the filled foam sheet to remove volatile substituents from the active material introduced into said support member.

55. The method of claim 52 including introducing active negative material containing finely divided lithiated carbon powder, or introducing active positive material containing lithiated metallic oxide powder, into said sheet of copper metal foam.

56. The method of claim 52 wherein said active material is introduced into said sheet form electrode support member of copper metal foam by one or more of spray application, pressure application or vacuum application.

57. The method of claim 52 further comprising compressing said electrode in sheet form containing said material in said sheet, in the direction of the thickness thereof.

58. An electrode for a lithium-ion secondary battery produced by the method of claim 52.

59. A method of producing a negative electrode for an alkaline secondary battery, comprising the steps of:

providing a large pore copper metal foam negative electrode support member having a pore size of larger than about 80 pores per inch and a weight of less than about 420 grams per square meter;

establishing said large pore copper metal foam in sheet form, with the resulting sheet form electrode support member having a thickness within the range from about 0.75 millimeter to about three millimeters; and

introducing active negative material into said sheet form electrode support member of large pore copper metal foam to produce a negative electrode in sheet form containing said material in said sheet.

60. A negative electrode for an alkaline secondary battery produced by the method of claim 59.

61. A method of producing a negative electrode for an alkaline secondary battery, comprising the steps of:

providing a large pore nickel metal foam negative electrode support member, with said support member having a pore size of larger than abut 80 pores per inch and a weight of less than about 700 grams per square meter;

establishing said large pore nickel metal foam in sheet form, with the resulting sheet form electrode support member having a

thickness within the range from about 0.75 millimeter to about three millimeters; and

introducing active negative material into said sheet form electrode support member of large pore nickel metal foam to produce a negative electrode in sheet form containing said material in said sheet.

62. The method of claim 61 further comprising drying the filled foam sheet to remove volatile substituents from the active negative material introduced into said support member.

63. The method of claim 61 including introducing active negative material containing finely divided hydrogen-absorbing alloy powder into said sheet of large pore nickel metal foam.

64. The method of claim 61 wherein there is introduced negative active material into said electrode support member that comprises one or more of AB_2 type hydrogen storage alloy, AB_5 type hydrogen storage alloy, or a cadmium active material comprising cadmium metal.

65. The method of claim 63 wherein said finely divided alloy powder is sintered and said sintering is carried out at a temperature between about 800°C to about 1200°C for a time of from about five minutes to about two hours.

66. The method of claim 61 wherein said negative active material is introduced into said sheet member of large pore nickel metal foam by one or more of spray application, or pressure or vacuum application.

67. The method of claim 61 further comprising compressing said filled foam sheet in the direction of the thickness thereof.

68. A negative electrode for an alkaline secondary battery produced by the method of claim 61.

69. The negative electrode of claim 68 for a metal hydride alkaline secondary battery.

70. The negative electrode of claim 68 for a nickel cadmium alkaline secondary battery.

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(54) Title: METAL FOAM SUPPORT MEMBER FOR SECONDARY BATTERY ELECTRODE

(57) Abstract

A copper metal foam, or a large pore size metal foam, particularly a large pore size nickel metal foam, is utilized as a support for a negative electrode in a metal hydride alkaline secondary battery. Or a copper metal foam is employed as a support for an electrode of alithium–ion secondary battery. The metal foam for the electrode support is a light weight, typically very flexible foam. The metal foam is particularly serviceable as an electrode support for a hydrogen storage alloy negative electrode, e.g., an electrode containing an active material of metallic alloy, such as an AB_5 class of alloy or an AB_2 class of alloy. As a support for an alkaline secondary battery negative electrode, the large pore metal foam may also serve as the negative cadmium electrode for a nickel–cadmium battery. As copper metal foam, the foam may further serve as the support for the positive or negative electrode, or for both, for a lithium–ion secondary battery.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/20163

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M4/24 H01M4/02 H01M4/80

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 044 (E-710), 31 January 1989 -& JP 63 239771 A (MATSUSHITA ELECTRIC IND CO LTD), 5 October 1988, see abstract -& CHEMICAL ABSTRACTS, vol. 110, no. 10, 6 March 1989 Columbus, Ohio, US; abstract no. 79376, KAWANO ET AL: "Paste type hydrogen-absorbing battery anodes" XP002059589 see abstract ---	1,3,8,9, 11,43, 45-47, 49,51 45,47-50

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 97/20163

Box I Observati ns wh r certain claims wer found unsearchable (Continuation of it m 1 of first sh t)

This international Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

SEE ADDITIONAL SHEET

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [X] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

1-11, 22-30, 43-51, 52-58, 59, 60

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[X] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-11, 43-51,
   59-
   60(as related to electrodes comprising hydrogen-absorbing metal alloy)

   Negative hydrogen-absorbing metal alloy electrode having a copper foam support, method for producing and battery

2. Claims: 12-21, 43-45, 47, 49, 50,
   59-60(as related to cadmium electrodes)

   Negative cadmium electrode having a copper foam support, method of producing and battery

3. Claims: 22-30, 52-58

   Electrode for lithium-ion secondary battery having copper foam support, method of producing and battery

4. Claims: 31-42, 61-70

   Negative hydrogen-absorbing metal alloy electrode or cadmium electrode having a nickel foam support with the same features of porosity, weight and thickness, method of producing and battery

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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